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MAR 30 2007

Substitute Specification & Abstract
U.S.S.N. 09/863,324

A PROTECTIVE FILM TRANSFER SHEET FOR PHOTOMASKS
AND A METHOD FOR TRANSFERRING A PROTECTIVE FILM
USING THE SAME

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims, under 35 USC 119, priority of Japanese Application No. 2000-154453 filed May 25, 2000.

BACKGROUND OF THE INVENTION

[0002] The present invention relates to a protective film transfer sheet for photomasks. In particular, it relates to a transfer sheet for transferring a protective film suitable for protecting copies for photomechanical processing or copies of printed wiring boards, which are susceptible to damage, and to a method for transferring a protective film using the transfer sheet.

[0003] A surface protective film comprising a thin plastic film such as a polyethylene terephthalate film, as a support, and a releasing film laminated on the plastic film via a self-adhesive or bonding agent has been used for protecting copies of photomechanical processing and printed wiring boards, which are susceptible to damage. When the surface protective film is used for photomasks, the releasing film is peeled off from the support and the surface is coated with a self-adhesive or bonding agent and laminated onto the image surface of a photomask.

[0004] In recent years, patterns formed on photomasks, which are copies used for photomechanical processing and in manufacture of printed wiring boards, have become

complicated and are required to have a high resolving power. This has raised demand for thinner protective films. However, if the surface protective film having the aforementioned structure is made too thin, its workability in laminating onto photomasks becomes poor, and wrinkles and cells are likely to be produced.

[0005] In order to improve such protective films, Japanese Utility Model Publication No.6-20601, for example, discloses a multiple layer sheet for use in transfer of a protective film which comprises a plastic film having an uneven surface, an abrasion resistant film formed on the uneven surface, an easy-release sheet having a self-adhesive layer and a releasing layer formed on the abrasion resistant film. Another transfer sheet comprising a release sheet, a resin layer cured by exposure to UV or electron beam and an adhesive layer consisting of an ionizing radiation curable resin formed on the releasing surface of the releasing sheet in this order is also known (Japanese Patent Unexamined Publication No. 63-132097).

[0006] However, when the generally used self-adhesive is employed as in the disclosure of Japanese Utility Model Publication No. 6-20601, the transferred protective layer is insufficiently resistant to marring, even if it has a sufficient hardness, because of softness of the self-adhesive layer. In addition, if it is used for protection of photomasks for printed wiring boards, another problem is encountered. That is, photo-resist may stick to the surface of the protective layer and require removal by using organic solvents. However, the protective film has low resistance to solvents and, therefore, has low durability.

[0007] The adhesive layer consisting of an ionizing radiation curable resin as disclosed in Japanese Patent Unexamined Publication No. 63-132097 is likely to lose adhesiveness when the thickness is too small. If the protective film with extremely low adhesiveness is used for

protection of a photomask in manufacture of a printed wiring board, the adhesive layer separates from the image surface of the photo mask when the photo mask is peeled from the photo-resist on the board. Thus, the protective layer has low durability. Further, if the adhesive layer consists of an ionizing radiation curable resin alone, fluidity of the adhesive layer becomes too high, and workability becomes poor because the adhesive layer is likely to be pressed out upon laminating.

SUMMARY OF THE INVENTION

[0008] The present invention aims at solving the above-mentioned problems. An object of the present invention is to provide a protective film transfer sheet for photomasks capable of providing a protective film, which is excellent in adhesiveness to the image surface of photomasks, in mar resistance and in resistance to solvents when transferred to photomasks. Another object of the present invention is to provide a method for transferring a protective film using the transfer sheet, which is capable of providing a protective film excellent in adhesiveness to the image surface of photo masks, mar resistance and resistance to solvents when transferred to photo masks.

[0009] Accordingly, the present invention provides a protective film transfer sheet which comprises a peelable support and a protective film formed on the support, wherein the protective film comprises a protective layer and an adhesive layer formed on the support in this order and the adhesive layer has pressure-sensitive adhesiveness, the adhesiveness of the adhesive layer being increased by heat imparted after it is transferred onto the image surface of a photomask, and is curable by exposure to ionizing radiation.

[0010] In the protective film transfer sheet of the present invention, the adhesive layer contains at least an ionizing radiation curable resin and a heat-reactive resin.

[0011] In the protective film transfer sheet of the present invention, the heat-reactive resin is preferably an acrylic copolymer containing a monomer having a heat-reactive functional group(s).

[0012] In the protective film transfer sheet of the present invention, the heat-reactive functional group(s) is preferably a hydroxyl group.

[0013] In the protective film transfer sheet of the present invention, the preferred monomer having a hydroxyl group is N-methylol acrylamide monomer.

[0014] In a preferred embodiment of the protective film transfer sheet for photomasks of the present invention, the ionizing radiation curable resin consists of a paint containing one or more kinds of photopolymerizable prepolymers or photopolymerizable monomers which can be crosslinked and cured by exposure to ionizing radiation, and at least one of a photopolymerizable prepolymer or photopolymerizable monomer having a hydroxyl group.

[0015] A method for transferring a protective film in accordance with the present invention, which uses the above-described protective film transfer sheet for transferring a protective film onto the image surface of a photomask, comprises the steps of:

- (1) adhering the adhesive layer of the protective film transfer sheet onto the image surface of a photomask,
- (2) heating the adhesive layer,
- (3) exposing the adhesive layer to ionizing radiation, and
- (4) peeling off the support from the protective film.

[0016] In the method for transferring a protective film of the present invention, the steps (1) and (2) are preferably performed simultaneously and thereafter the steps (3) and (4) are performed in this order.

[0017] According to the present invention, there is provided a protective film transfer sheet capable of providing a protective film which is excellent in adhesiveness to the image surface of photomasks, in mar resistance and in resistance to solvents when transferred onto photomasks.

BRIEF DESCRIPTION OF THE DRAWING

[0018] Fig. 1 is a sectional view of an example of a protective film transfer sheet of the present invention.

PREFERRED EMBODIMENTS OF THE INVENTION

[0019] The protective film transfer sheet of the present invention is described in further detail with reference to the attached drawing.

[0020] As shown in Fig. 1, the protective film transfer sheet 1 of the present invention includes a protective film 3 consisting of a protective layer 31 and an adhesive layer 32 and, as occasion demands, a separator 4, *on a peelable support 2*
is laminated to adhesive layer 32
formed on a peelable support 2.

[0021] The support 2 of the present invention is a base material on which the protective layer 31 and adhesive layer 32 are laminated successively and facilitates transfer of a thin protective film 3 onto the image surface of a photomask.

[0022] Although the support 2 is not particularly limited, it is preferably transparent to ionizing radiation so that the adhesive layer 32 can be exposed to ionizing radiation through the support 2 and cured. A transparent plastic film such as a polyethylene terephthalate film, polycarbonate film, polypropylene film, polyethylene film, polyvinyl chloride film, polyethylene naphthalate film, or polystyrene film may be used for the support 2. A biaxially stretched film is preferable for its excellent mechanical strength, heat resistance and dimensional stability. The thickness of the support 2 is preferably 5-125 μm to facilitate handling.

[0023] In order to improve release of the support 2 from the protective layer 31, a plastic film 21 having a release layer 22 may be used for the support 2.

[0024] The release layer 22 remains on the surface of the plastic film 21 after transferring the protective film 3 and allows the support 2 to be easily removed. Material of the release layer may be selected from melamine resins, silicone resins, amino alkyd resins, urethane resins, urea resins, epoxy resins, fluorine resins, polyvinyl alcohol resins, polyvinyl methylether/maleic acid anhydride copolymers, and so forth taking into account combination with the protective layer 31. Among them, water-soluble resins such as polyvinyl alcohol resins, polyvinyl methylether/maleic acid anhydride copolymers and the like are preferable from the viewpoint of ease of release and ease of laminating.

[0025] When the transferred surface is required to be uneven, the release layer 22 may include matting agents. In order to improve adhesiveness to the plastic film 21, an easy adhesive layer may be provided between the release layer 22 and the plastic film 21.

[0026] The protective layer 31 is required to have high mar resistance and resistance to solvents, because the protective layer 31 becomes the uppermost layer of the protective film after

it is transferred to the image surface of a photomask and, therefore, its properties directly affect those of the protective film 3.

[0027] The protective layer 31 having such high mar resistance and resistance to solvents can be obtained by applying a composition consisting of a thermosetting resin or an ionizing radiation curable resin onto the support 2 using a known coating technique and curing it.

[0028] Usable thermosetting resins include resins crosslinkable by heat such as silicone resins, melamine resins, epoxy resins, amino alkyd resins, urethane resins, acrylic resins, polyester resins, phenol resins. These resins may be used alone but are preferably mixed with a hardening agent in order to improve crosslinking and hardness of the crosslinked film.

[0029] The ionizing radiation curable resin is composed of a paint crosslinkable and curable at least by exposure to ionizing radiation (ultraviolet ray or electron beam). As the ionizing radiation curable paint, a mixture of one or more kinds of photopolymerizable prepolymers or photopolymerizable monomers may be used.

[0030] Usable photopolymerizable prepolymers include various kinds of (meth)acrylates such as polyester (meth)acrylate, epoxy (meth)acrylate, urethane (meth)acrylate, polyether (meth)acrylate, polyol (meth)acrylate, melamine (meth)acrylate.

[0031] Examples of the photopolymerizable monomer include styrene monomers such as styrene, α -methyl styrene, (meth)acrylate esters such as methyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, methoxyethyl (meth)acrylate, butoxyethyl (meth)acrylate, butyl (meth)acrylate, methoxybutyl (meth)acrylate, phenyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, ethoxymethyl (meth)acrylate, lauryl (meth)acrylate, unsaturated carboxylic acid amides such as (meth)acryl amide, substituted amino alcohol esters of unsaturated acid such as 2-(N,N-

diethylamino)ethyl (meth)acrylate, 2-(N,N-dibenzylamino) ethyl (meth)acrylate, 2-(N,N-diethylamino)propyl (meth)acrylate, multifunctional compounds such as ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, nonaethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, tetrapropylene glycol di(meth)acrylate, nonapropylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol tri(meth)acrylate, pentaerythritol hexa(meth)acrylate, trimethylolpropane (meth)acrylate, glycerol tri(meth)acrylate, tris-(2-hydroxyethyl)-isocyanuric acid ester (meth)acrylate, 2,2-bis[4-(acryloxy diethoxy) phenyl] propane, 3-phenoxy-2-propanoyl acrylate, 1,6-bis (3-acryloxy-2-hydroxypropyl)-hexyl ether, and polythiol compounds having two or more thiol groups per molecule such as trimethylol propane trithioglycolate, trimethylol propane trithiopropylate, pentaerythritol tetrathioglycolate.

[0032] Various additives can be added to the ionizing radiation curable paint. When UV is used for curing, it is preferable to add a photopolymerization initiator, UV intensifier or the like. Usable photopolymerization initiators include acetophenones, benzophenones, Michler's ketone, benzoin, benzylmethylketal, benzoyl benzoate, α -acryloxy ester, thioxanthenes and the like. As the UV intensifier, n-butylamine, triethylamine, tri-n-butylphosphine and the like can be used.

[0033] Examples of conventional coating methods for applying the aforementioned thermosetting resin or ionizing radiation curable resin to the support include knife coating, doctor coating, bar coating, roll coating, blade coating, kiss-roll coating, spray coating, spin coating, dip coating and the like.

[0034] The adhesive layer 32 of the present invention is adhered to the image surface of a photomask by its pressure-sensitive adhesiveness at normal temperature. The adhesiveness to the image surface of a photomask increases by heating after the layer 32 is adhered. In addition, when the adhesive layer 32 is cured by exposure to ionizing radiation, the adhesiveness and the hardness of the layer 32 also increase.

[0035] Such an adhesive layer 32 contains an ionizing radiation curable resin and a heat-reactive resin.

[0036] The aforementioned paint for the protective layer 31, which is crosslinkable and curable by exposure to ionizing radiation (ultraviolet ray or electronbeam), can be used for the ionizing radiation curable resin of the adhesive layer 32. Photopolymerizable prepolymers or photopolymerizable monomers used for the ionizing radiation curable paint are preferably those having a hydroxy group(s).

[0037] When the adhesive layer 32 is formed using a mixture of an ionizing radiation curable paint containing the photopolymerizable prepolymers or photopolymerizable monomers having a hydroxy group(s) and a heat-reactive resin consisting of an acrylic copolymer containing a monomer having a hydroxy group, such as an N-methylol acrylamide monomer, the hardness of the adhesive layer 32 can be improved by reaction of ionizing radiation curable resins with the heat-reactive resins and the adhesiveness to the image surface of the photomask is also increased.

[0038] Examples of the the photopolymerizable prepolymers or photopolymerizable monomers having a hydroxy group(s) include pentaerythritol tri(meth)acrylate and 1, 6-bis (3-acryloxy-2-hydroxypropyl)-hexylether.

[0039] Similarly to the aforementioned paint for the protective layer 31, the ionizing radiation curable paint may contain photopolymerization initiators, UV intensifiers and the like.

[0040] Reaction of the heat-reactive resin proceeds with heating after the adhesive layer 32 is adhered to the photomask, at the interfaces between the adhesive layer 32 and protective layer 31 and between the adhesive layer 32 and the image surface of the photomask, so that the adhesiveness at the interfaces is increased. Generally, the thermal reaction of the heat-reactive resins also increases the hardness of the adhesive layer 32.

[0041] The heat-reactive resin consists of an acrylic copolymer having a heat-reactive functional group as a monomer component. Such an acrylic copolymer can be a copolymer of (meth)acrylate monomer and a monomer having a heat-reactive functional group.

[0042] Examples of the (meth)acrylate monomer include ethyl (meth)acrylate, butyl (meth)acrylate, amyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, cyclohexyl (meth)acrylate, benzyl(meth)acrylate and the like. One or more of these monomers can be used in a mixture.

[0043] Examples of monomers having a heat-reactive functional group include monomers having a carboxy group such as (meth)acrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid, monomers having a hydroxy group such as 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, N-methylol acrylamide, aryl alcohol, monomers having a ^{tertiary} amino group such as dimethyl aminoethyl(meth)acrylate, diethylaminoethyl (meth)acrylate, dimethyl aminopropyl(meth)acrylate, monomers having an amide group such as (meth)acrylamide, a monomer having a N-substituted amide group such as N-methyl (meth)acrylamide, N-ethyl (meth)acrylamide, N-methoxymethyl (meth)acrylamide,

N-ethoxymethyl (meth)acrylamide, N-t-butyl acrylamide, N-octyl acrylamide, monomers having an epoxy group such as glycidyl(meth)acrylate. Among them, monomers having a hydroxy group such as an N-methylol acrylamide are particularly preferred for obtaining excellent adhesiveness to the object on which the adhesive layer 32 of the present invention is transferred, i.e., the image surface of a photomask. It is considered that, when a monomer having a hydroxy group is used for the adhesive layer 32, the monomer reacts with hydroxy groups in the image surface of the photomask to increase the adhesiveness. This strong adhesion between the protective film 3 and the image surface of a photomask prevents the protective film 3 from separating from the image surface during working and, thereby, workability is improved.

[0044] The ratio of the monomers of the acrylic copolymer, i.e., a (meth)acrylate monomer, and monomer having a heat-reactive functional group, is 1-2.5 weight parts, preferably 5-15 weight parts of the monomer having a heat-reactive functional group per 100 weight parts of the (meth)acrylate monomer.

[0045] The weight average molecular weight of the acrylic copolymer is preferably 50,000-2,000,000, more preferably 100,000-1,000,000.

[0046] Other monomers can be copolymerized in the acrylic copolymer, provided the characteristics of the copolymer are not compromised.

[0047] Examples of such other monomers, which can be copolymerized, include vinyl acetate, styrene, methyl styrene, vinyl toluene, acrylonitrile, (meth)acrylamide, N-methyl acrylamide and so forth. The ratio of these monomers is generally 0-30 weight parts, preferably 0-15 weight parts, per 100 weight parts of the sum of the (meth)acrylate monomer and monomer having a heat-reactive functional group.

[0048] The mixing ratio of the constituents of the adhesive layer 32, the ionizing radiation curable resin and the heat-reactive resin, is preferably 5-200 weight parts of the heat-reactive resin per 100 weight parts of ionizing radiation curable resin. When the heat-reactive resin is at least 50 weight parts, the adhesive layer is not pressed out during the transfer and high adhesiveness to the image surface of photomasks can be achieved. Thereby, workability is improved. When the heat-reactive resin is not more than 200 weight parts, sufficient hardness can be imparted to the adhesive layer 32 after it is exposed to ionizing radiation, and mar resistance and resistance to solvents of the protective layer 3 are also improved.

[0049] In the present invention, the heat-reactive resin provides initial bond strength of the adhesive layer 32 to the image surface of a photomask, and adhesiveness of the transferred protective film 3. The ionizing radiation curable resins provides adhesiveness to the image surface of the photomask and hardness of the transferred protective film 3 and, as a result, improves mar resistance and resistance to solvents of the protective film 3.

[0050] The thickness of the protective film 3 is preferably 1-20 μm . Sufficient mar resistance and resistance to solvents can be achieved with a thickness of not less than 1 μm . When the thickness is not more than 20 μm , a fine resolution pattern can be obtained in developing without problems. The thickness of each of the protective layer 31 and adhesive layer 32 is preferably 0.5-15 μm and may be suitably varied provided the thickness of the protective film 3 does not exceed its upper limit. When the thickness of the adhesive layer is not less than 0.5 μm , sufficient adhesiveness to the image surface of the photomask and mar resistance can be obtained. When the thickness is not more than 15 μm , the protective film is sufficiently thin to provide a high resolution pattern.

[0051] The separator 4 is provided so that the workability is not lowered by adhesiveness of the adhesive layer 32. The material of the separator 4 may be a plastic film such as a polyester film, a polyethylene film, a polypropylene film and so forth, or paper coated with a release agent such as a silicone.

[0052] The protective film transfer sheet 1 can be manufactured, for example, as follows: a protective layer 31 and an adhesive layer 32 are formed successively on a support 2, consisting of a release layer 22 on a polyethylene terephthalate film 21 which transmits ionizing radiation, and a separator 4 is laminated to the adhesive layer 32.

[0053] A method of transferring a protective film will be explained in detail hereinafter.

[0054] The method for transferring a protective film of the present invention, which uses the above-mentioned protective film transfer sheet, comprises the steps of:

- (1) adhering the adhesive layer of the protective film transfer sheet onto the image surface of a photo mask,
- (2) heating the adhesive layer,
- (3) exposing the adhesive layer to ionizing radiation, and
- (4) peeling off the support from the protective film.

[0055] In order to transfer a protective film having excellent adhesiveness to the image surface of a photomask, mar resistance and resistance to solvents, which are features of the present invention, step (1) should be performed first. In order to improve ease of transfer, it is preferable to carry out the steps (1) and (2) simultaneously.

[0056] If the performance of the transferred protective film is considered to be most

important, however, the step (2) is not necessarily performed simultaneously with the step (1). It may be performed in any order relative to steps (3) and (4) but is preferably performed prior to steps (3) and (4) in order to increase adhesiveness to the image surface of the photomask.

[0057] Steps (3) and (4) are performed in an arbitrary order but the step (3) is preferably performed prior to step (4) in order to protect the protective layer with the support until the adhesive layer becomes sufficiently hard.

[0058] In step (1), the adhesive layer of the protective film transfer sheet may be laminated to the image surface of a photomask in the following manner: the separator, which is provided as occasion demands, is peeled off, and then the protective film transfer sheet may be laminated to the image surface of a photomask using a laminator with the adhesive layer in contact with the image surface.

[0059] In step (2), heating the adhesive layer, heat may be imparted (conducted) through the support or photomask using a heat roll as the laminator roll used in step (1) so that step (2) is performed simultaneously with step (1). Alternatively, after the adhesive layer is laminated using a laminator roll without imparting heat, heat is imparted to the layer by means of a heat roll, by placing in a hot environment such as an oven with internal air circulation, or by exposure to far infrared rays. Although the temperature of the heat roll is not particularly limited because the quantity of heat imparted to the adhesive layer varies depending on the nip pressure of the roll and the conveying speed, it may be suitably selected from within the range of 40-150°C, preferably 60-120°C in terms of surface temperature.

[0060] By heating the adhesive layer in such a manner after the transfer sheet is laminated, its adhesiveness to the image surface of the photomask is increased.

[0061] In step (3) of exposing the adhesive layer to ionizing radiation (UV or electron beam), UV can be applied using an ultra-high-pressure mercury-vapor lamp, high-pressure mercury-vapor lamp, low-pressure mercury-vapor lamp, carbon arc, metal halide lamp or the like. An Electron beam can be applied using an electron accelerator such as a Cockcroft-Walton type, Van de Graff type, transformer type, isolated core transformer type, Dynamitron type, high-frequency type and so forth.

[0062] By increasing the hardness of the adhesive layer by exposure to ionizing radiation in such a way, mar resistance and resistance to solvents of the protective film can be improved.

[0063] In step (4), the support is peeled off from the protective film 3 to complete transfer of protective film 3 to the image surface of the photomask.

EXAMPLES

[0064] Examples of the present invention will be now described, which should not be construed as limiting the present invention. In the examples, "part" and "%" are based on weight unless otherwise, defined.

1. Synthesis of a heat-reactive resin

[0065] 3.0g of N-Methylol acrylamide monomer, 84.0g of n-butyl acrylate monomer, 5.0g of 2-hydroxyethyl methacrylate monomer, 3.0g of acrylic acid monomer, 5.0g of ethyl acrylate monomer, 36.0g of ethyl acetate, 12.0g of toluene, 12.0g of isopropyl alcohol and 0.10g of α, α' -azobis(isobutyronitrile) were added to a reactor having a stirrer, a condenser, a

thermometer, and a duct for introducing nitrogen, and stirred and heated at 75°C while introducing nitrogen. The reaction solution was maintained at 75°C for 8 hours while stirring to complete the reaction and to synthesize an acrylic copolymer, which is a heat-reactive resin. 45.0g of ethyl acetate and 45.0g of isopropyl alcohol were added to the reaction solution to prepare a heat-reactive resin solution (A) containing 40.0% nonvolatiles.

2. Preparation of a protective film transfer sheet for photomasks

Example 1

[0066] A coating solution for a release layer having the following composition was applied to one side of a polyethylene terephthalate film 21 having a thickness of 50 μm (T-600E: Mitsubishi chemical Polyester Film Co., Ltd.), and dried to obtain a support 2 provided with a release layer 22 having a thickness of about 1 μm .

Coating solution for release layer

-Polyvinyl methylether/maleic acid anhydride copolymer (GANTREZ AN119:ISP Co., Ltd.)	50 parts
-Distilled water	414 parts
-Meta-modified alcohol	36 parts

[0067] Then, a coating solution for the protective layer and a coating solution for an adhesive layer (a) having the following compositions were applied successively on the release layer 22 of the support 2 and dried to form a protective layer having a thickness of about 2 μm and an adhesive layer having a thickness of about 2 μm . After the protective layer 31 dried, it

was cured by exposure to UV using a high-pressure mercury lamp. The release surface of a separator 4 (E7006: Toyobo Co., Ltd.) having a thickness of 38 μm was laminated to the adhesive layer 32 to obtain a protective film transfer sheet having the structure shown in Fig.1.

Coating solution for protective layer

- Urethane acrylate (UniDic V4005, solids content 64%:
Dainippon Ink & Chemicals Inc.) 125 parts
- Photopolymerization initiator (Irgacure 184:
Ciba Specialty Chemicals K.K.) 2.4 parts
- Toluene 275 parts

Coating solution for adhesive layer (a)

- 1, 6-Bis(3-acryloxy-2-hydroxypropyl)-hexyl ether 16 parts
- Photopolymerization initiator (Xrgacure 907:
Ciba Specialty chemicals K.K.) 1.2 parts
- Heat-reactive re-sin solution (A) 80 parts
- Ethyl acetate 232 parts
- Toluene 232 parts

[0068] The separator 4 was peeled off from the thus obtained protective film transfer sheet 1 and the adhesive layer 32 was laminated to the image surface of a photomask having a circuit wiring pattern formed on a silver salt film (AGX-7: Kodak Co., Ltd.) using a laminator

equipped with a heat roll at 100°C. Then, the adhesive layer was cured by exposure to 600mj/cm² of UV using a high-pressure mercury lamp and the support 2 was peeled from the protective film to transfer the protective film 3 to the image surface of the photomask.

Example 2

[0069] A protective film transfer sheet 1 was obtained in the same manner as in Example 1 except that a coating solution (b) was used for the adhesive layer instead of the coating solution (a). The protective film of this transfer sheet was transferred to the image surface of a photomask in the same manner as in Example 1.

Coating solution for adhesive layer (b)

-Hydropivalic acid neopentyl glycol diacrylate	16 parts
-Photopolymerization initiator (Irgacure 907: Ciba Specialty Chemicals K.K.)	1.2 parts
-Heat-reactive resin solution (A)	80 parts
-Ethyl acetate	232 parts
-Toluene	232 parts

Comparative Example 1

[0070] A protective film transfer sheet was obtained in the same manner as in Example 1 except that a coating solution was used for the tacky layer instead of the coating solution (a) for an adhesive layer.

Coating solution for tacky layer

- Self-adhesive acrylic resin (SK dyne1102, solid content
40%: Soken Chemical and Engineering Co., Ltd.) 30 parts
- Isopropyl alcohol 75 parts

[0071] The separator was peeled off from the thus obtained protective film transfer sheet and the tacky layer was laminated to the image surface of a photomask having a circuit wiring pattern formed on a silver salt film (AGX-7: Kodak Co., Ltd.) using a laminator. Then, the support was peeled from the protective film to transfer the protective layer and the tacky layer to the image surface of the photomask.

Comparative Example 2

[0072] A protective film transfer sheet was obtained in the same manner as in Example 1 except that a coating solution (c) was used for the adhesive layer instead of the coating solution (a).

Coating solution for adhesive layer (c)

- Urethane acrylate (UniDic V4005, solids content 64%:
Dainippon Ink & Chemicals Inc.) 20 parts
- Dipentaerythritol hexaacrylate (Kayarad PDHA:
Nippon Kayaku Co., Ltd.) 8 parts
- Photopolymerization initiator (Irgacure 651:

Ciba Specialty Chemicals K.K.)	1 parts
-Methylethyl ketone	35 parts
-Toluene	35 parts

[0073] The separator was peeled off from the thus obtained protective film transfer sheet and the adhesive layer was laminated to the image surface of a photomask having a circuit wiring pattern formed on a silver salt film (AGX-7: Kodak Co., Ltd.) using a laminator. Then, the adhesive layer was cured by exposure to 600mj/cm² of UV using a high-pressure mercury lamp and the support was peeled from the protective film to transfer the protective layer and the adhesive layer to the image surface of the photomask.

[0074] For the protective film transfer sheets obtained in Examples 1, 2 and Comparative Examples 1, 2, mar resistance, pencil hardness, adhesiveness, and resistance to solvents of the protective film transferred to the image surface of the photo mask were evaluated. The results are shown in Table 1.

Table 1

	Mar resistance (Load)		Pencil hardness	Adhesiveness	Resistance to solvents
	150 g	300 g			
Example 1	◎	◎	H	100/100	○
Example 2	○	○	H	95/100	○
Comparative example 1	×	×	2 B	80/100	×
Comparative example 2	○	△	H B	0/100	×

Mar resistance (resistance to marring)

[0075] The surface of the protective layer 31 was rubbed back and forth ten times with steel wool #0000 under a load of 150g or 300g, and marring of the surface was evaluated visually, criteria of the visual evaluation were as follows:

- ◎ : No marring was produced.
- : very slight marring was produced.
- △ : Marring was produced.
- X : Marring was produced throughout the surface.

Pencil hardness

[0076] Pencil hardness was evaluated based on the pencil hardness test according to JIS-K5400. Specifically, the transferred protective film was scratched by a pair of pencils having successive density codes. A pair in which one pencil tore the film twice or more and the other pencil tore the film less than twice was found, and the density code of the pencil that tore the film less than twice was defined to be the pencil hardness of the film.

Adhesiveness

[0077] Adhesiveness was evaluated by the crosscut adhesion tape method according to JIS-K5400. Specifically, the film was crosscut to make a hundred lattices with an interval of 1 mm. A cellophane tape defined by JIS-Z1522 was adhered to the film and then peeled from the film. After the tape was peeled, the state of the film was observed and the number of lattices which were not peeled off was recorded.

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